SN 10/730978

PTO 05-[2933]

Japanese Patent

Hei 2-190483

Translation of

JP 2-190483

GALVANIZED STEEL PLATE WITH EXCELLENT PRESS MOLDABILITY

[Puresu Seikeisei Ni Sugureta Aenmekki Koban]

Tetsuya Nomoto and Takashi Hotta

UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C. April 2005

Translated by: Schreiber Translations, Inc.

Country	:	Japan
Document No.	:	Hei 2-190483
Document Type	:	Kokai
Language	:	Japanese
Inventor	:	Tetsuya Nomoto and Takashi Hotta
Applicant	:	Nippon Steel Corporation
~~IPC~~	~~:~~	~~C 23 C 28/00~~
Application Date	:	January 19, 1989
Publication Date	:	July 26, 1990
Foreign Language Title	:	Puresu Seikeisei Ni Sugureta Aenmekki Koban
English Title	:	GALVANIZED STEEL PLATE WITH EXCELLENT PRESS MOLDABILITY

/1[1]

Specification

1. Title of the invention

Galvanized Steel Plate with Excellent Press Moldability

2. Claims

1. A galvanized steel plate with excellent press moldability, characterized by the fact that an oxide film is formed on the surface of a galvanized steel plate.

2. A galvanized steel plate with excellent press moldability, characterized by the fact that an oxide film mainly composed of ZnO is formed at an amount of ZnO of 30-3,000 mg/m^2 (per one surface) on the surface of a galvanized steel plate.

3. A method for manufacturing the galvanized steel plate with excellent press moldability of Claim 1, characterized by the fact that an oxide mainly composed of zinc or iron is formed on the plated layer surface of the galvanized steel plate by electrolytic oxidation, immersion oxidation, or spreading oxidation treatment.

[1] Numbers in the margin indicate pagination in the foreign text.

4. A method for manufacturing the galvanized steel plate with excellent press moldability of Claim 2, characterized by the fact that after the plated layer surface is changed to a solid phase state or the plated layer surface is alloyed and roughened, it is heated, so that an oxide film mainly composed of ZnO is formed.

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3. <u>Detailed explanation of the invention</u>

(Industrial application field)

The present invention pertains to a galvanized steel plate with excellent press moldability.

(Prior art and problems to be solved by the invention)

It has already been known that the press moldability is degraded in galvanized steel plates, compared with cold-rolled steel plates. It is considered that the cause for this is due to the constraint of the deformation of a base iron by the plated layer. Also, as a means for improving the press moldability of the galvanized steel plate, a method that spreads various kinds of lubricants with a high viscosity on the surface of the galvanized steel plate is generally broadly adopted. However, this method requires a work for spreading the lubricants before the press molding and a degreasing work after the press molding. For this reason, in addition to the increase

of the cost, the environment of a press work site is deteriorated.

Also, as shown in Japanese Kokai Patent Application No. Sho 62[1987]-185883, a chromium oxide or Fe-Zn plating is applied to the surface of the galvanized steel plate having a soft plated layer, and the surface is hardened, so that a mold scuffing during the press molding is avoided. /2

However, in avoiding the press fracture phenomenon that represents the press moldability, the effect cannot be expected only by giving a hard coated film. As an anticorrosive reinforcing measure of various kinds of press-moldable products, though various kinds of galvanized steel plates are frequently used, the development of a galvanized steel plate with excellent press moldability is strongly in demand as the industrially most effective means.

The present invention favorably solves such a demand and provides a galvanized steel plate that can greatly improve the press fracture during press-molding.

(Means to solve the problems)

The present invention pertains to (1) a galvanized steel plate with excellent press moldability characterized by the fact that an oxide film is formed on the surface of a galvanized steel plate; (2) a galvanized steel plate with excellent press

moldability characterized by the fact that an oxide film mainly composed of ZnO is formed at an amount of ZnO of 30-3,000 mg/m^2 (per one surface) on the surface of a galvanized steel plate; (3) a method for manufacturing the galvanized steel plate with excellent press moldability characterized by the fact that an oxide mainly composed of zinc or iron is formed on the plated layer surface of the galvanized steel plate by electrolytic oxidation, immersion oxidation, or spreading oxidation treatment; and (4) a method for manufacturing the galvanized steel plate with excellent press moldability characterized by the fact that after the plated layer surface is changed to a solid phase state or the plated layer surface is alloyed and roughened, it is heated, so that an oxide film mainly composed of ZnO is formed.

(Operation)

In other words, the material fracture being generated during press-molding is caused when the fracture proof stress of the material exceeds the inflow resistance force of the material. The inflow resistance force of the material consists of a sliding resistance force being generated between a mold die and a blank holding pad in addition to a deformation resistance of the material. Therefore, in order to reduce the inflow resistance force of the material, it is effective to reduce the

sliding resistance force. The sliding resistance force is generated when a relative slip is caused in the contact part of the mold and the material. The sliding resistance force consists of a collapse force of the convex part of the material surface and a frictional force of the contact part of the mold and the material. It has been known that if an oil film exists at the interface where the material and the mold contact, the frictional force is largely reduced, and in the press molding, usually, a low-viscosity oil having a primary antirust is usually used. In the low-viscosity oil, if the contact surface pressure of the mold and the material is high, the oil film is broken, and the mold and material are directly contacted, so that the frictional force is increased. In this state, the holding performance of the oil film is important for suppressing the increase of the frictional force. In other words, in the present invention, as mentioned above, it was discovered that if an oxide film existed on the surface of a galvanized steel plate, the adsorption power of the oil film was increased and the oil film could be held under a high surface pressure, even in a low-viscosity oil such as antirust oil, so that the increase of the frictional force could be effectively suppressed.

Then, as the galvanized steel plate, there are galvanized steel plates formed by various kinds of manufacturing methods such as melt-plating method, electroplating method, vapor deposition plating method, and thermal spraying method, and as the plating composition, in addition to pure Zn, like Zn and Fe, Zn and Ni, Zn and Al, and Zn and Mn, Zn is used as a main component, and one kind or two kinds or more of alloy elements and impurity elements are included to improve the functions such as corrosion resistance. Also, fine ceramic particles such as SiO_2 and Al_2O_3, oxides such as TiO_2, organic polymers dispersed into a plating layer, single composition in the thickness direction of a plating layer, and composition with a continuous or layered change are used. Furthermore, the uppermost layer has Fe and Ni as main components and can include various kinds of alloy elements such as Zn and P. For example, there are melt-galvanized steel plate, iron-zinc alloyed melt-galvanized steel plate, alloy melt-galvanized steel plate such as aluminum and iron having zinc as a main component, alloyed melt-galvanized steel plate (generally called a half alloy) in which the lower layer is alloyed in the sectional direction of the plated layer), steel plate in which one surface is an iron-zinc alloyed melt-galvanized layer and the other surface is a melt-galvanized layer, steel plate in which a metal such as zinc,

iron, and nickel is plated on these plated layers by electroplating, vapor deposition plating, etc., electric galvanized steel plate, alloy electric galvanized steel plate of zinc, nickel, chromium, etc., single alloy layer or multilayer alloy electroplated steel plate, plated steel plate in which an organic film is coated on these plated layers, vapor-deposited plated steel plate of zinc and metal containing zinc, etc. In addition, there is a dispersed plated steel plate in which /3 fine ceramic particles such as SiO_2 and Al_2O_3, TiO_2 oxide fine particle, organic polymer, etc., are dispersed into a zinc or zinc alloy plating.

These inventors found out that if an oxide film was formed on the surface of a plated steel plate, regardless of the kind of galvanized steel plate, the inflow resistance force of the material could be markedly reduced in press-molding.

Next, as an oxide being formed on the surface of the galvanized steel plate, constitutional components or compounds such as its oxides being included in the plated layer may also be included in addition to ZnO in the oxide. Also, in an electrochemical treatment such as anodic oxidation, components or compounds containing a treatment solution may be included.

The amount of such an oxide being generated is 30-3,000 mg/m^2 as an amount of ZnO (pre one surface) in the oxide. If the

amount of ZnO is less than 30 mg/m^2, the effect is small, and if the amount exceeds 3,000 mg/m^2, the chemical treatment is difficult, which is not preferable.

Such an oxide can be reliably detected by dissolving the plated layer with 5% iodine methanol solution, for instance, melting the extracted residue in a mixed melting agent (boric acid 1, sodium carbonate 3), solubilizing it with hydrochloric acid, and converting the amount of zinc analyzed by an ICP into an amount of ZnO. Also, the oxygen integrated intensity value for 1 sec from the uppermost layer measured by a glow discharge spectroscopy (GOS) is 1.0-10 VS (per one surface).

As mentioned above, the ZnO film may also be formed only one surface of the galvanized steel plate, however in order to effectively reduce the sliding resistance force, the treating surface may be set to a die side and press-molded. In order to obtain a further effect, the moldability can be further raised by forming the films on both surfaces.

Then, as a method for generating the above-mentioned oxide, in case the uppermost plated surface is a solid-phase state or the plated layer is heated and alloyed, the alloying is advanced, and the roughness of the surface is completed (the uppermost surface is in a single layer state of ζ or δ phase or a state in which both of them are mixed or a state in which η

phase exists partially), and the oxide mainly composed of ZnO can be reliably formed by the reaction with water at high temperature.

As its detailed method, for example, in a continuous melt-galvanizing, there is an alloying furnace in the line, and an alloying treatment is carried out in the alloying furnace by heating in combination with dew point adjustment, etc. After completing the alloying, the oxide can be reliably generated while applying a steam spray and a vapor spray or by reacting at high temperature in a high dew point atmosphere. As a heat treatment condition, at a dew point of 0°C, heating for 2 sec or more at a heating temperature of 350°C or higher is sufficient. Needless to say, in case the dew point can be maintained further high, a sufficient amount of oxide can be obtained in a low-temperature or short-time treatment.

Furthermore, as methods for forming the oxide, an immersion oxidation method in an alkali or acid solution after plating, a method that oxidizes these solutions by roll-coating or spraying, an electrochemical oxidation method in an alkali, neutral, or acid solution, etc., are effective means.

(Application examples)

Application examples of the present invention are shown along with comparative examples in Table I.

Table I

項目 / 実施態様	めっき鋼板の種類	目付量 (g/m²) 片面/他面	酸化膜形成法	酸化膜量 (片面/他面) ZnO (mg/m²)	酸素強度 O: (V.S)	摺動抵抗係数 (R) 片面/他面
実施例 1	Gi 両面	50/50	A	110/120	1.3/1.3	0.55/0.60
実施例 2	片面AS,他面Gi	40/80	A	130/70	1.4/1.1	0.52/0.62
実施例 3	AS 両面	100/100	A	110/130	1.3/1.4	0.48/0.50
実施例 4	AS 両面	70/70	A	150/170	1.5/1.6	0.45/0.50
実施例 5	AS 両面	70/70	B	1200/1100	4.4/4.2	0.35/0.34
実施例 6	AS 両面	60/60	A	60/75	1.0/1.1	0.42/0.46
実施例 7	AS 両面	45/45	AA	300/250	2.4/2.0	0.43/0.43
実施例 8	AS 両面	60/60	AA	280/300	2.2/2.4	0.46/0.47
実施例 9	AS 両面	80/80	AA	310/280	2.4/2.4	0.47/0.48
実施例10	AS-E 両面	35/60	B	70/85	1.1/1.2	0.33/0.44
実施例11	ZL-E 両面	23/23	B	65/75	1.0/1.1	0.30/0.33
実施例12	EG 両面	60/60	C	1800/1900	6.3/6.4	0.65/0.63
実施例13	エクセライト	23/23	B	1400/1500	4.6/4.7	0.32/0.30
実施例14	ジンクライト	20/20	B	950/750	4.0/3.8	0.48/0.52
比較例 1	AS 両面	70/70	—	20/15	0.3/0.3	0.80/0.88
比較例 2	Gi 両面	50/50	—	10/12	0.2/0.2	0.90/0.98
比較例 3	AS-E 両面	30+3/60	—	23/18	0.4/0.3	0.50/0.87
比較例 4	ZL-E 両面	20+3/20+3	—	17/18	0.3/0.3	0.52/0.55
比較例 5	エクセライト	23/23	—	12/13	0.2/0.2	0.53/0.55
比較例 6	ジンクライト	20/20	—	17/21	0.3/0.4	0.75/0.80
比較例 7	EG 両面	20/20	—	17/21	0.3/0.4	0.99/0.95

1. Item
2. Kind of plated steel plate
3. Amount of Metsuke (g/m2), one surface/the other surface
4. Method for forming an oxide film
5. Amount of oxide film (one surface/the other surface)
6. Sliding resistance coefficient (R), one surface/the other surface
7. Oxygen intensity O: (V.S)
8. Embodiment
9. Application Example
10. Comparative Example
11. Gi both surfaces

12. One surface AS, the other surface Gi

13. AS both surfaces

14. AS-E both surfaces

15. ZL-E both surfaces

16. EG both surfaces

17. Excelite[transliteration]

18. Zinclite[transliteration]

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19. AS both surfaces

20. Gi both surfaces

21. AS-E both surfaces

22. ZL-E both surfaces

23. Excelite

24. Zinclite

25. EG both surfaces

Note 1): As the kind of plated steel plate, AS: Melt iron-zinc alloyed plated steel plate (after melt-galvanizing, heat-treated, 7-13% iron, the balance zinc), Gi: Melt galvanized steel plate, EG: Electric galvanized steel plate, Excelite: electroplated steel plate of a lower layer of 15% iron and the balance zinc (amount of Metsuke: 20 g/m^2) and an upper layer of

85% iron and the balance zinc (amount of Metsuke: 3 g/m^2), Zinclite: Electroplated steel plate of 12% nickel and the balance zinc (amount of Metsuke: 20 g/m^2), AS-E: 85% iron and the balance zinc (amount of Metsuke: 3 g/m^2) are electroplated on the upper layer of the melt iron-zinc alloyed plated steel plate (AS), ZL-E: 85% iron and the balance zinc (amount of Metsuke: 3 g/m^2) are electroplated on the upper layer of 12% nickel and the balance zinc (Zinclite). The thickness of these steel plates is usually 0.80 mm.

Note 2): As the method A for forming an oxide film, for Gi, the surface was set to a solid-phase state after melt-galvanizing and heated at 350°C for 10 sec in an air atmosphere. For ASH, it was heated at a plate temperature of 530°C for 12 sec after melt-galvanizing, and right after the completion of the roughness of the surface, it was heated at 400°C for 3 sec. In any cases, the thickness of the oxide films was adjusted by adjusting the dew point (0-100°C) of the plate surface by a vapor spray.

Note 3): In the method AA for forming an oxide film, a steam spray method was used as a method for adjusting the dew point (0-100°C) of the plate surface in the method A.

Note 4): In the method B for forming an oxide film, an oxide film was formed by an immersion method into an acid solution after plating.

Note 5): In the method C for forming an oxide film, an oxide film was formed by a cathode treatment method into a bath containing zinc ions and an oxidizer after plating.

Note 6): The sliding resistance coefficient was quantified under the following conditions. The material was ultrasonic-washed with an acetone solution and sufficiently degreased, and the sliding resistance coefficient was attained by the method shown in Figure 1. Its measurement conditions are as follows.

In Figure 1, 1 is a contactor, 2 is a load, 3 is a load cell, 4 is a specimen, 5 is a die, and 6 is a motor for moving the contactor. F is a sliding resistance force.

Contactor (1): SKD11, quenched material with a diameter of

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Load (P) (2): 1 kgf /5

Moving speed of contactor: 2.8 mm/sec

Moving distance of contactor: 80 mm

The sliding resistance force, as shown in Figure 1, was measured via the load cell installed at the contactor. A measurement example is shown in Figure 2. The sliding resistance force F was changed as shown in the figure with the sliding distance by the friction state of the contact surface. Here, the average of the minimum and maximum sliding resistance

forces (F: kgf) was adopted, and the sliding resistance coefficient (R) was defined by the following equation.

$$R = F/P$$

Note 7) Measurement of ZnO in an oxide film

Only the plated layer was dissolved with 5% iodine methanol solution, and the extracted residue was melted with a mixed melting agent (boric acid 1, sodium carbonate 3), and solubilized with hydrochloric acid. The amount of zinc analyzed by an ICP was converted into ZnO.

Note 8): Oxygen intensity (oxygen intensity of an oxide film)

The integrated intensity value of oxygen for 1 sec from the uppermost surface measured by a glow discharge spectroscopy (GDS)

Note 9): NOx530F40 (trade name) made by Parker Kyosan K.K. was spread at 1 g/m^2 on the steel plate surface in both the application examples and the comparative examples.

(Effects of the invention)

In this manner, the inflow resistance force of the material during press-molding can be largely reduced, so that the fracture inferiority phenomenon of the molded product was reduced, thereby being able to greatly improve the productivity.

Also, the yield of the press-molded product can be markedly improved.

4. <u>Brief description of the figures</u>

Figure 1 is an illustrative diagram showing a moldability tester, and Figure 2 is an illustrative diagram showing the relationship between the sliding resistance and the sliding distance.

1 Contactor

2 Load

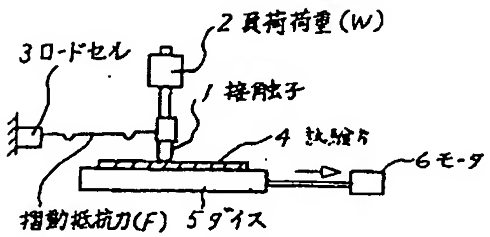
3 Load cell

4 Specimen

5 Die

6 Motor

第 1 図



第 2 図

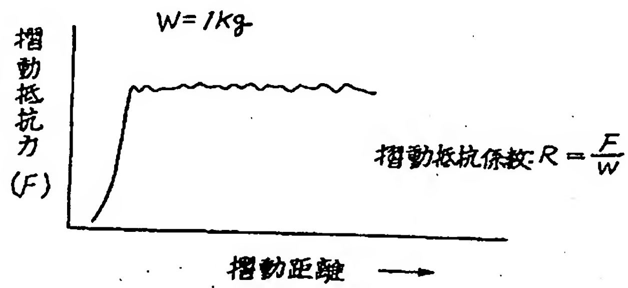


Figure 1:

1 Contactor

2 Load

3 Load cell

4 Specimen

5 Die

6 Motor

A. Sliding resistance force (F)

Figure 2:

1. Sliding resistance force (F)

2. Sliding distance

3. Sliding resistance coefficient: $R = F/W$